Nanosphere Lithography Using Thermal Evaporation of Gold

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Abstract — Nanosphere lithography, which allows for the fabrication of patterned metal surfaces, is a simple, effective and unconventional technique that exploits a self-assembly process. Using this technique, polystyrene nanospheres with diameters of 500nm, and 1µm were assembled onto a 'muscovite' mica substrate in a hexagonally close packed monolayer array, to provide a physical mask for material deposition. Thermal evaporation was subsequently used to deposit gold through the nanosphere mask layer, to generate a periodic array of gold nanostructures. Upon changing the mask to a multi-layered array of nanospheres, slightly more complex nanostructures were achieved. However due to thermal evaporation being a high temperature process the nanostructures obtained deviated from their predicted quasi triangular shape due to a slight annealing of the polystyrene mask.

Keywords - Nanosphere lithography; Surface patterning

I. INTRODUCTION

The fabrication of surfaces that exhibit nanoscale variations in their chemical properties, namely, nano-patterned metallic surfaces have received increasing attention in nanotechnology [1] due to their potential application in biosensors [2, 3], data storage [4], photonics [3], catalysis and etching masks [5]. A variety of techniques have been developed for generating patterned surfaces including photolithography, electron beam lithography, and scanning probe lithography [1, 2, 4]. These techniques are limited by issues such as precise control of the chemical composition, size, shape and distribution of the created nanofeatures as well as high-cost, low throughput production of the patterned surface [1]. It is very difficult to produce well-defined, large area, nano-patterned surfaces at low cost [2, 5]. For example, the most widely used technique, photolithography, has not been widely applied to nanostructures as a consequence of diffraction limited resolution, $\lambda/2$, where λ is the wavelength of incident photons [5]. Greater spatial resolution can be achieved via electron beam and scanning probe lithography, both of which are capable of producing nanoscale features down to ~5nm. However the patterned areas that these techniques can typically produce do not usually exceed 1mm^2 [4]. These techniques are also inherently slow and costly.

Recently, colloidal nanosphere lithography has emerged as a simple, effective, low cost and versatile substrate patterning technique [4] that is capable of producing periodic arrays of metallic dots that range from 20-200nm in size [2] and of theoretically vast areas.

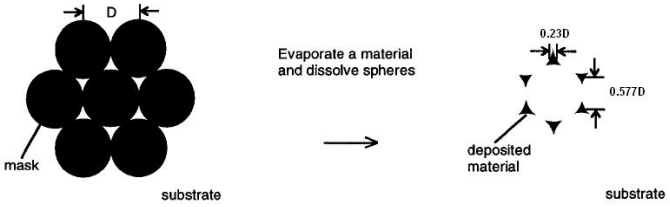

Figure 1. Nanosphere lithography mechanism [6].

Monodispersed nanosphere colloids, usually polystyrene, can be assembled onto a flat surface, forming a close-packed monolayer with hexagonal symmetry and a quasi triangular void space existing among the three spheres in physical contact with each other as shown in figure 1 [6]. The monolayer can then serve as a physical mask through which metals or dielectric materials can be deposited onto the underlying substrate. Upon removal of the colloid nanospheres, typically by dissolution, periodic arrays of nanometre-sized metal islands remain. The lateral dimensions of the metal islands can be controlled by changing the colloidal nanosphere diameter; the vertical dimensions primarily dependent upon the amount of material that is deposited through the mask. One aspect, which makes this approach very appealing, is that the resulting nanostructures are approximately one fifth of the size of the colloidal nanospheres. Hence it is possible to generate nanometre-sized structures from micrometre-sized colloidal spheres [6, 7]. The major problem with nanosphere lithography, however, is the lack of control over defects, dislocations and the size of 2D nanosphere crystal domains [6]. The patterns generated are also very limited in terms of their design and complexity, as it is difficult to independently change the lateral dimensions of features and the separation between them [7].

Typically, techniques such as sputter coating and electron beam evaporation [2, 8, 9] are used to deposit material through the void space of the polystyrene mask, resulting in a quasi-triangular array of nanostructures as shown in figure 1. Much work has then been done towards the growth of carbon nanotubes on metallic catalyst arrays generated from nanosphere lithography [2, 8, 10]. For the growth of single walled carbon nanotubes round catalysts are required with the diameter of the nanotube being directly proportional to the catalyst particle size [2]. Hence additional steps such as ammonia plasma etching or high temperature annealing of the quasi triangular nanostructures is required to obtain an array of round nanostructures [8, 10]. With the use of thermal evaporation the polystyrene nanosphere mask can be annealed during material deposition resulting in round nanostructures in one step.

II. Materials & Methods

Drop coating and solvent evaporation was employed to fabricate monolayer and multilayer coverage of nanospheres on a 'Muscovite' mica substrate. Mica was used as the substrate due to the ease with which comparatively large atomically flat, hydrophilic, regions can be created through cleavage. Monodispersed surface modified polystyrene nanosphere suspensions with nominal diameter of 500nm and 1μm were purchased from Fluka Production GmbH. The concentration of the suspensions was 2% wt polystyrene nanospheres in D_2O. Two drops of the polystyrene nanosphere suspension was applied to the surface of a 1cm x 2cm mica wafer. The nanosphere solution was then further diluted drop wise in a 1:1 v/v ratio with a 1:400 v/v solution of the surfactant Triton-x-100 and methanol [11]. Increasing the hydrophilicity of the polystyrene nanospheres in such a way aids in the convective self-assembly of the hexagonally close packed 2D colloidal crystal upon evaporation, allowing for better packing over large areas [11]. Upon addition of Triton-x-100 to the substrate the polystyrene nanospheres can be seen to immediately disperse over the mica surface. After holding the substrate stationary for 1 minute, allowing for a good dispersion of the suspension, the mica wafer was slowly immersed (mica held vertically) into a petri dish of HPLC grade water produced by a MilliQ Plus system from Millipore with a resistivity of 18MΩcm [12]. Upon contact with the water's surface an unordered layer of nanospheres was observed to form on both the water and mica surface. The mica wafer was then slowly withdrawn from the water and orientated horizontally whilst the suspension evaporated resulting in monolayer coverage of hexagonally close packed periodic nanosphere arrays. By increasing the concentration of polystyrene nanosphere suspension placed onto the mica wafer to 4 drops and following the same procedure it was possible to create regions of multi-layers. Once assembled, a 2nm platinum coating was sputtered onto nanosphere array and scanning electron microscopy then used to image the hexagonally close packed colloidal crystal using a Philips XL30 Field Emission Scanning Electron Microscope.

Gold was deposited onto the nanosphere masked mica substrate using a vacuum deposition method based on thermal evaporation by resistance. Approximately 0.025g of annealed 24 carat yellow fine gold foil was placed into a piece of 0.25mm thick 99.9% molybdenum foil bent into a boat-like shape. The chamber then sealed and evacuated for 15 minutes allowing for a pressure of 10^{-5} torr to be obtained. A low current was then applied to the boat allowing for any contaminants absorbed on the gold or boat surface to evaporate onto a rotatable shield. The shield was then rotated out of the direct path between the boat and substrate prior to the current being increased, allowing the gold to evaporate onto the substrate.

After gold deposition the polystyrene nanosphere mask was removed by gentle ultrasonication of the entire mica wafer in absolute ethanol for 5 minutes. The polystyrene was observed to dissolve and come away from the mica surface as a white cloud in the ethanol. Prolonged or vigorous sonication would result in the de-lamination of the gold from the mica surface. Atomic Force Microscopy using a multi-mode head and Nanoscope IV controller, Digital Instruments, Veeco, Santa Barbara, operating in tapping mode with a FESP-ESP series cantilever with fundamental resonance frequency between 70-85 KHz was used to image the resulting gold nanostructures.

III. Discussion

Upon imaging the assembled monolayer of polystyrene nanospheres 500nm and 1μm in diameter the quasi-triangular voids in a honeycomb lattice can clearly be seen. Figure 2 a) and b) show the 500nm spheres, c) and d) show the 1μm spheres. The individual nanosphere size, spacing between quasi-triangular void spaces and size of the perpendicular bisector of each nanostructure in the array can be seen in e) and f)

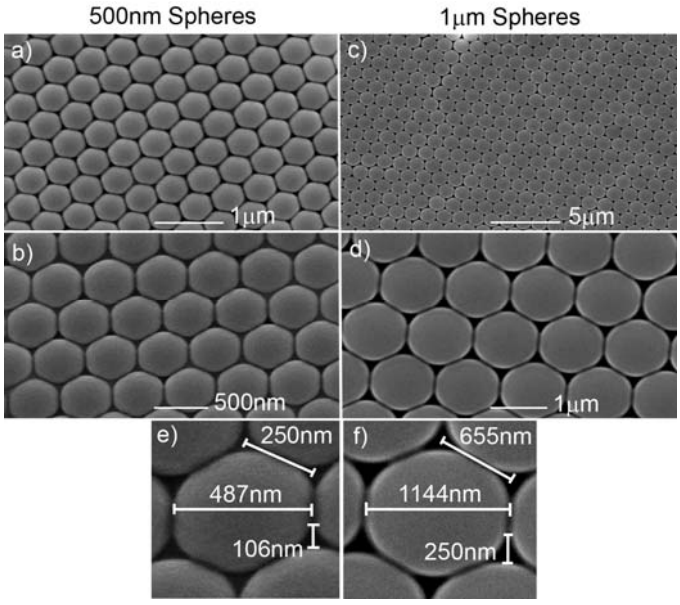

Figure 2. SEM image of monolayer self assembled polystyrene nanospheres on a mica surface

By increasing the nanosphere concentration it is possible for multi-layers of nanospheres to form. Spheres in the second layer acquire the lowest energy packing with respect to the first, arranging with AB packing. When a second

layer of nanospheres assembles onto the first, every other three-fold hole is covered and a smaller density of six fold interstices results, a pattern of hexagonal holes is generated [13]. Subsequent layers can take one of two possible arrangements, the nanospheres can pack in an ABAB configuration in which case the hexagonal hole mask is maintained or in an ABCABC configuration in which case all mask holes are blocked rendering the polystyrene nanosphere mask useless for substrate patterning [13].

After gold deposition and removal of the polystyrene nanospheres by dissolution two different types of nanostructure patterns where observed on the mica substrate. An array of gold nanostructures due to monolayer and multi-layer nanosphere masks respectively as can be seen by AFM in figure 3.

Immediately it can be seen that the nanofeatures obtained are in fact a distorted circular shape instead of quasi-triangular as expected. This is attributed to a slight annealing of the polystyrene nanosphere mask upon gold deposition resulting in a slight closure of the void spaces. This effect has previously been observed upon microwave annealing of the polystyrene mask as shown in figure 4 [9].

Polystyrene mask annealing occurring due to thermal evaporation by resistance being a high temperature, low energy process. To a degree, the annealing is controllable by altering the deposition time and temperature, however, due to the limitations in the vacuum evaporator design this is difficult to achieve accurately. Radiant heat from the molybdenum boat, which is at a temperature approximately the melting point of gold, 1064 °C, is also often enough to anneal the polystyrene nanosphere mask, melting point of 240 °C. For this reason low temperature, high energy processes such as sputter coating and electron-beam evaporation are normally used for material deposition in nanosphere lithography.

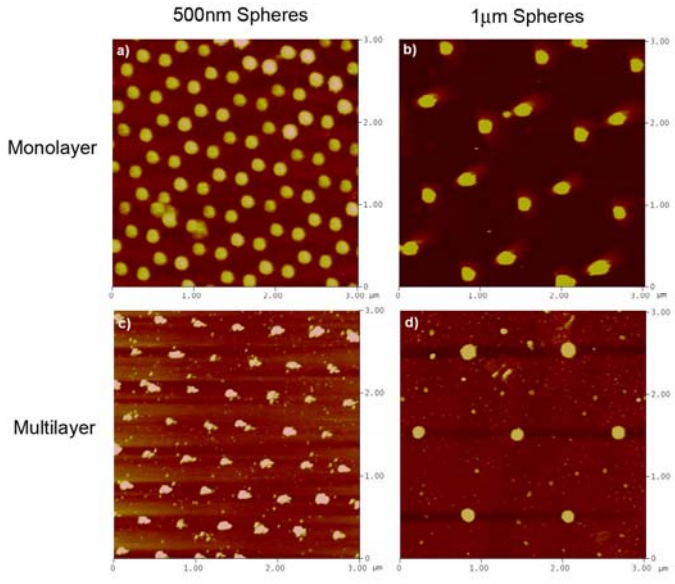

Figure 3. AFM image of gold nanostructures on mica due to a) 500nm, b) 1µm nanosphere monolayer mask, c) 500nm d) 1µm ABAB packed multilayer nanosphere mask

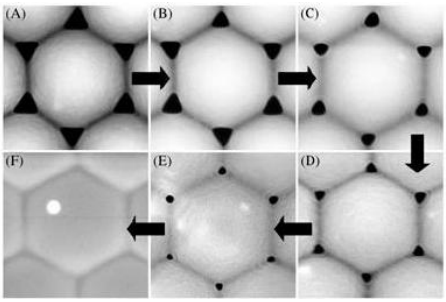

Figure 4. 540nm polystyrene nanosphere mask annealed by a) 1, b) 2, c) 4, d) 6, e) 7 and f) 10 microwave pulses, resulting in decreased void sizes [9].

In the simplest scenario a monolayer of polystyrene nanospheres are assembled in a hexagonally close packed way onto the mica substrate, generating quasi-triangular void spaces for metal deposition. Geometric calculations define the relationship between the perpendicular bisector of the largest possible equilateral triangle that will fit amongst spheres in physical contact, a, and the inter-particle spacing, d_{ip}, to the nanosphere diameter, D [13].

$$a = \frac{3}{2}\left(\sqrt{3} - 1 - \frac{1}{\sqrt{3}}\right)D \qquad d_{ip} = \frac{1}{\sqrt{3}}D$$

As with the single layer, geometrical calculations define the relationship between the diameter of the hexagonal nanoparticles, a, and the interparticle spacing, d_{ip}, to the nanosphere diameter, D [13].

$$a = \left(\sqrt{3} - 1 - \frac{1}{\sqrt{3}}\right)D \qquad d_{ip} = D$$

Figure 5 shows AFM line scans of the gold nanofeatures generated by the two size nanospheres, indicating the obtained particle dimensions, all values have not been de-convoluted for tip broadening effects and are hence overestimations of the particle size. Figure 5 a) and c) are the patterns generated from monolayer coverage of 500nm and 1µm spheres respectively, the gold nanostructured pattern closely resembling what would be expected from a nanosphere mask annealed to the extent of figure 4 c), d) or e). Figure 5 b) and d) are the patterns from multi-layer assembled nanospheres of size 500nm and 1µm respectively and circular nature of the nanostructures is seen to increase. Table 1 summarises the expected size and separation of individual nanostructures from both SEM and the geometric calculations and compares them to the obtained dimensions from AFM. The AFM dimensions obtained by taking an average of 19 measurements and the de-convoluted dimensions calculated using a modification of the method described by Xu et al. [14].

The expected numbers in table 1 assume the perfect nanosphere layer as described in the formula or observed after formation via SEM, continues to exist during the evaporation. The size of the features observed via AFM will be too large due to the convolution of feature size and the radius of curvature of the tip. This effect can be deconvoluted out with a knowledge of the tip shape based on the method of Xu et al.

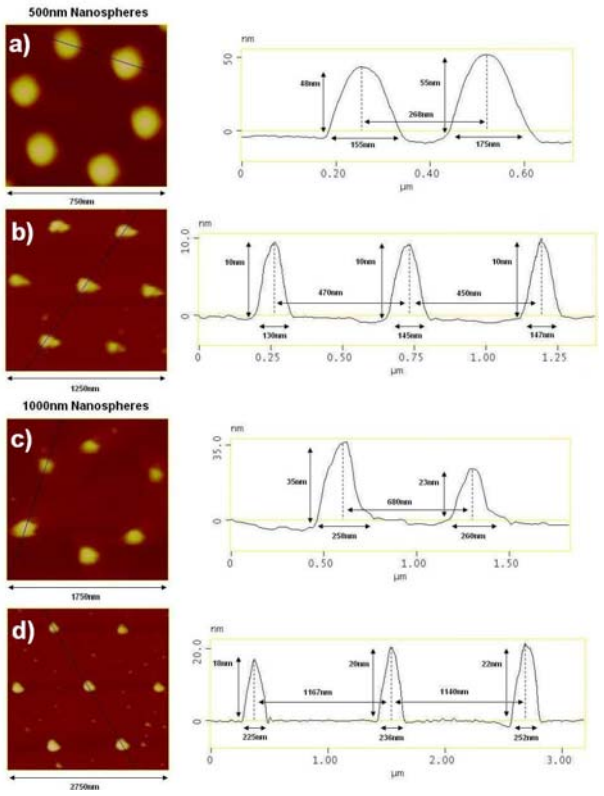

Figure 5. AFM line scans indicating the dimensions of the gold nanoparticles generated by nanosphere lithography

The deconvoluted sizes are the true sizes of the features made during the evaporation of the gold through the mask. They are smaller than the expected sizes due to the annealing of the mask. As the spheres anneal, the voids decrease in size and hence yield smaller metallic features. The reduction of feature sizes is slightly greater in terms of a percentage of the expected size in the case of the multiple layers. This is expected as the annealing in two layers will lead to a more rapid decrease in void size and a greater reduction in feature size. With better control of the heat load on the sample this could be exploited to yield patterned metallic substrates with very small sizes of the individual components of the pattern.

AFM imaging does yield correct numbers for feature separation as the central point of the feature will be unchanged regardless of the tip geometry. Hence there is no need to correct the separation values obtained from AFM and these agree quite well with predicted values. The vertical height of the feature, especially for a hard structure such as a gold dot, will also be unaffected by tip geometry.

IV. Conclusion

Nanosphere lithography has been shown to be a simple, convenient, low cost and highly reproducible technique to generate nanometre sized metallic arrays on a surface. Polystyrene nanospheres of nominal 500nm and 1μm diameter have been assembled in a hexagonally close packed monolayer array onto a 'muscovite' mica substrate. Gold nanostructures 120-250nm in size over an area up to 100μm^2 were created. Due to the high temperature, low energy nature

	500nm Spheres			
	Monolayer		Multilayer	
	Nanostructure Diameter (nm)	Nanostructure Separation (nm)	Nanostructure Diameter (nm)	Nanostructure Separation (nm)
Expected, SEM	106	250		
Expected, Formula	112	280	75	487
Obtained, AFM	187 ± 14	274 ± 10	137 ± 11	430 ± 33
De-Convoluted, AFM	83	274	37	430
	1000nm Spheres			
	Monolayer		Multilayer	
	Nanostructure Diameter (nm)	Nanostructure Separation (nm)	Nanostructure Diameter (nm)	Nanostructure Separation (nm)
Expected, SEM	250	655		
Expected, Formula	260	660	176	1144
Obtained, AFM	267 ± 21	704 ± 31	244 ± 24	1169 ± 34
De-Convoluted, AFM	147	704	90	1169

Table 1. Summary of expected and obtained nanostructure dimensions for monolayer and multilayer coverage of nanospheres.

of thermal evaporation slight annealing of the polystyrene nanosphere mask occurred, resulting in distorted circular nanostructures. The advantage of this approach is that the need for the normal subsequent step of annealing the patterned metallic dots in removed. Unfortunately, the low energy nature of thermal evaporation resulted in the gold-substrate adhesion energy being low and individual nanostructures were easily delaminated and displaced across the surface by sonication.

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